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New Lamination and Doping Concepts for Enhanced Lithium – Sulfur Battery Performance

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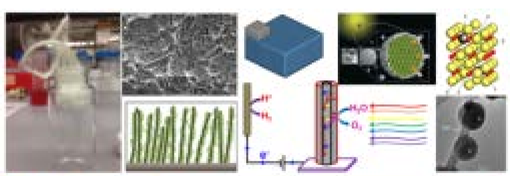
2016 DOE VEHICLE TECHNOLOGIES PROGRAM REVIEW

JUNE 6-10, 2016



NECST lab Driving innovation in battery and fuel cell materials
Nanomaterials for Energy Conversion & Storage Technology

Project ID #ES279

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Why Lithium-sulfur?

$S_8 + 16Li \leftarrow\rightarrow 8Li_2S$

Theoretical **specific capacity of ~1675 mAh/g**

Cathode voltage low (~1.5V-2.2 V wrt Li/Li^+)

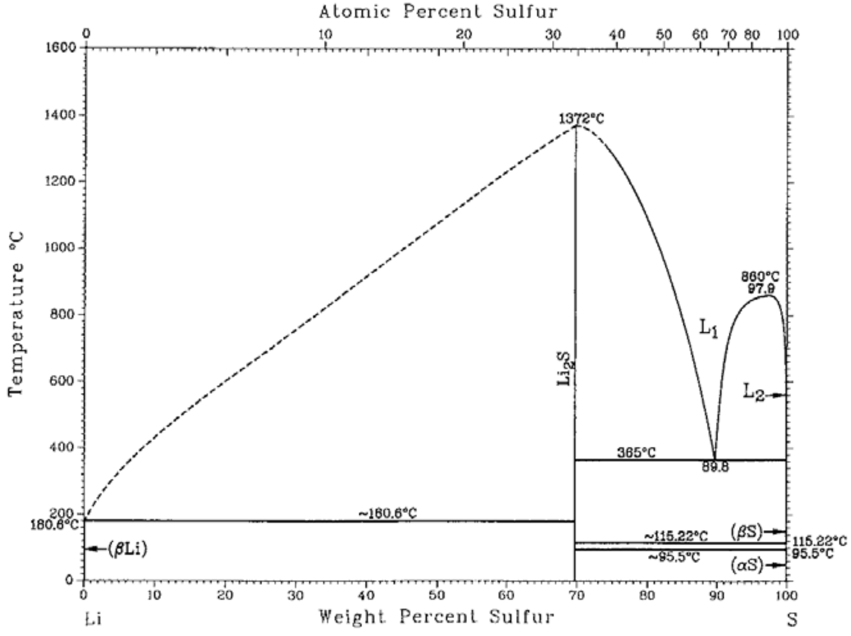
Energy density ~2567 Wh/kg

- Achievable: 500-600 Wh/kg

Low atomic weight of S (Light weight battery)

- Reduction in vehicle weight (largely determined by battery weight)
- Will reduce energy consumption

Li-S



Problems of Li-S battery chemistry

Negative electrode: Lithium

- Li: **dendrite formation**
- Safety issue

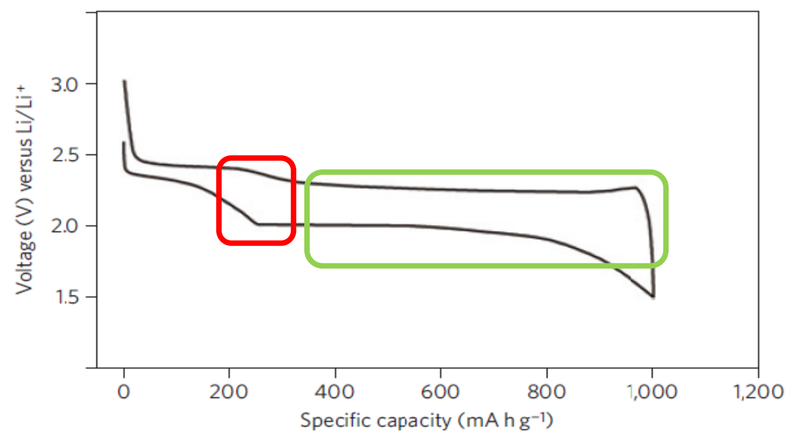
Positive electrode: Sulfur or sulfide

- Poor **electronic** and ionic conductivity of sulfur
- **Formation of polysulfide anions**
- **Polysulfide anions is soluble in electrolyte**
- Vol. expansion : 80%

Electrolyte: Li containing salt in organic solvent/ionic liquids

- Polysulfide attraction to solvent is high

Process	Reaction	Voltage	Kinetics	Solubility
Polysulfide formation	$Li+S \rightarrow Li_2S_x$; x=4-5	2.4 to 2.0 V	Extremely rapid	**Highly soluble**
Conversion to dilithium sulfide	$Li_2S_x \rightarrow Li_2S_2$ $Li_2S_2 \rightarrow Li_2S$	~2.0 V	**Sluggish kinetics**	Insoluble



Overview

Timeline

Start date: October 1, 2014

End date: September 30, 2017

Percent complete: 50%

Budget

- Total project funding: $1,250,061
  - DOE share: $1,250,061
  - Contractor share: $ 0
- Funding received in FY 2015: $416,687
- Funding for FY 2016: $416,687

Barriers addressed

- Low achievable energy density
- Polysulfide dissolution
- Cycling Stability
- Electronic conductivity
- Poor rate capability
- Surface passivation of both anodes and cathodes

Partners

- UPitt (S. Maiti, D. K. Achary)
- NETL (A. Manivannan)

Relevance for addressing barriers

- **Problems of sulfur:**
  - Poor cyclability:
  - Low columbic efficiency (CE)
  - Poor rate capability
  - Mechanical disintegration of the cathode
  - Surface passivation of both anode and cathode
- **Causes:**
  - Formation/dissolution of polysulfides
  - Sluggish kinetics of conversion of polysulfides to Li_2S
  - High diffusivity of polysulfides in the electrolyte
  - Insulating nature or poor conductivity of sulfur/Li_2S
  - Volumetric expansion/contraction of sulfur
  - Shuttling of polysulfides along with Li
- **Approaches:**
  - Preparation of sulfur nanoparticles (NP) for achieving high capacity
  - Coating of sulfur with Lithium ion Conductor (LIC) to prevent polysulfide dissolution
  - Modification of Sulfur nanoparticles to improve electronic conductivity
  - Composite LIC/sulfur nanoparticles to prevent dissolution
  - Use of framework materials to ensure polysulfide retention

Project Objectives

Overall Objectives

Energy Storage Performance Requirements		Electric Vehicle
Characteristics	Unit	
Specific Discharge Pulse Power	W/kg	700
Discharge Pulse Power Density	W/l	1,500
Specific Regen Pulse Power	W/kg	300
Recharge Rate	kW	1.4
Specific Energy	Wh/kg	350
Energy Density	Wh/l	750
Calendar Life	Year	15
Cycle Life	Cycles	1,000
Operating Temperature Range	°C	-30 to +52

- Synthesis and characterization of suitable LIC matrix materials and multilayer composite sulfur cathodes
- Development of LIC coated sulfur nanoparticles
  - Scale up of high capacity engineered LIC coated multilayer composite electrodes
- Modification strategies for improving electronic conductivity of sulfur
- Advanced high energy density, high rate, extremely cyclable cell development
- First principles calculations for LIC and dopant material identification

Project Objectives

Objectives (FY 2015)

Synthesis, Characterization and Scale up of suitable LIC matrix materials and multilayer composite sulfur cathodes (Target: design and development of baseline electrodes)

- Tailoring properties of LIC coating materials
  - Identify stable LIC materials
  - Use ab – initio first principle studies to identify dopants
  - Doping LIC to improve ionic and electronic conductivity
- Engineer LIC coating strategies using sputtering techniques
- Use of framework materials to ensure polysulfide retention

Objectives (FY 2016)

Development of LIC coated sulfur nanoparticles, scale up of high capacity engineered LIC coated multilayer composite electrodes and doping strategies for improving electronic conductivity of sulfur

- Synthesis and testing of modified sulfur nanoparticles
- Design and engineering of high capacity LIC coated sulfur nanoparticles for generation of high capacity materials for 4 mAh cell
- Develop interface engineering concepts and coating strategies to generate VACNT based multilayer composite electrodes of sulfur cathode

Milestones-FY 2015

Date	Type	Description	Status
January 2015	Milestone	Electrode and cell design parameters for achieving the PEV Target: ≥350Wh/Kg, ≥750Wh/l and 4 mAh full cell will be determined	Complete
July 2015	Milestone	Identify and synthesize coating materials with superior lithium ion conductivity and selectivity to avoid polysulfide solid-state diffusion and preparation of high capacity nanosulfur	Complete
October 2015	Milestone	Synthesize LIC coated multilayer composite electrodes with superior lithium ion conductivity and explore ideal morphologies to improve cycling stability	Complete
October 2015	Milestone	Perform first principles investigations into compositional modifications to improve electronic conductivity of sulfur	Complete
October 2015	Go/No-Go	75-100 μm thick electrodes will be designed, fabricated and tested in a coin cell configurations and compared to desired volumetric energy density requirements	Complete

Milestones-FY 2016

Date	Type	Description	Status
July 2016	Milestone	Fundamental electrochemical study to understand the interface electrochemical properties such as change of charge transfer resistance, Li^+ diffusivity and electronic conductivity	On-going
July 2016	Milestone	Develop interface engineering concepts and coating strategies of Phase-1 materials to generate VACNT based multilayer composite electrodes of sulfur cathode	On-going
October 2016	Milestone	Synthesis of modified sulfur nanoparticles with high electronic conductivity to reduce additive weight and increase energy density.	On-going
October 2016	Milestone	Design and engineering of high capacity LIC coated sulfur nanoparticles for generation of high capacity materials for targeted energy density and 4 mAh cell	On-going
October 2016	Go/No-Go	Synthesis of modified sulfur nanoparticles with high electronic conductivity to reduce additive weight and increase energy density	On-going

Approaches/Strategies

2015 April	May	June	July	Aug	Sep	Oct	Nov	Dec	2016 Jan	Feb	Mar
LIC coating - polysulfide trap				Identify stable and scalable LIC				**Test results**			
		Identify dopants using *ab – initio*				Synthesize doped LIC				**Tested – enhanced conductivity**	
				Strategies – Improve Sulfur Properties				Composite and framework approach		**Testing progress**	
						Engineered LIC coating techniques				**Establishing and optimizing techniques**	

Go/ No – Go decision point: The Go/ No – Go point was demonstrated by the ability to achieve three fold improvement in Li-ion conductivity of LIC materials.

Challenges and barriers: Techniques for effective LIC lamination of thick electrodes and of sulfur nanoparticles is currently ongoing

Technical accomplishments
Sulfur Nanoparticle synthesis

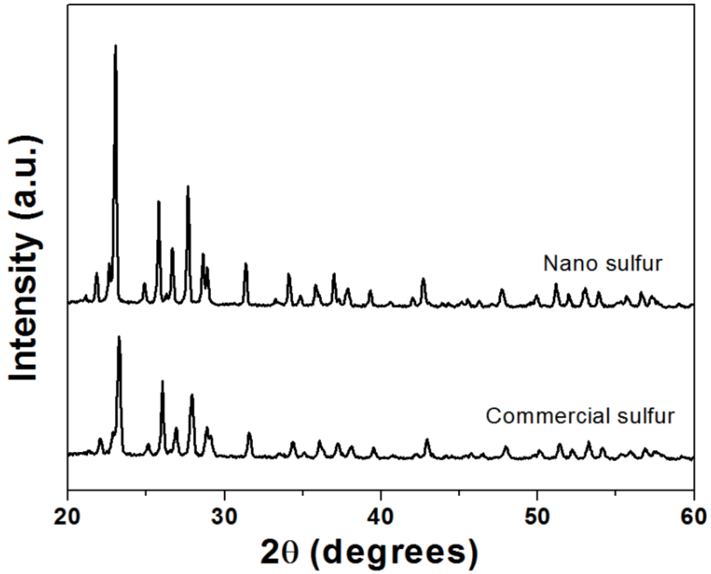
- Commercial sulfur is dissolved in hot boiling KOH at 110^0C

$$8S + 6KOH \rightarrow 2K_2S_3 + K_2S_2O_3 + 3H_2O$$

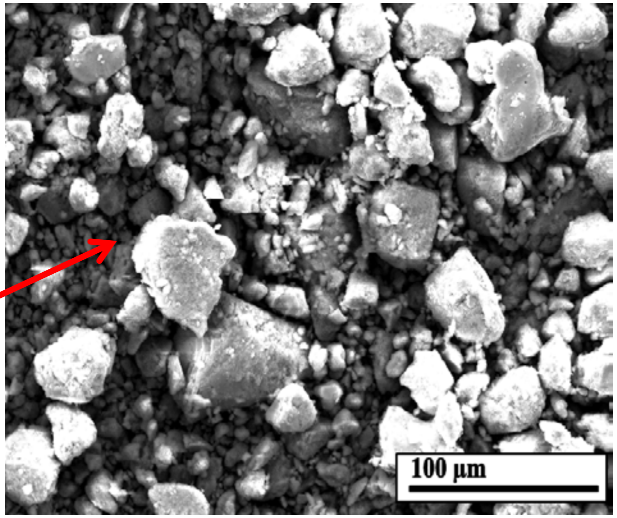
- Sulfur is precipitated by using HCl

$$K_2S_3 + 2HCl \rightarrow 2S\downarrow + 2KCl + H_2S\uparrow$$

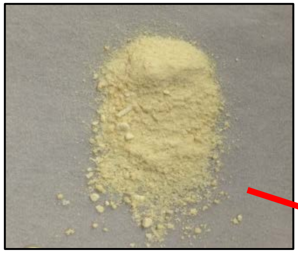
$$K_2S_2O_3 + 2HCl \rightarrow S\downarrow + 2KCl + H_2O + SO_2\uparrow$$

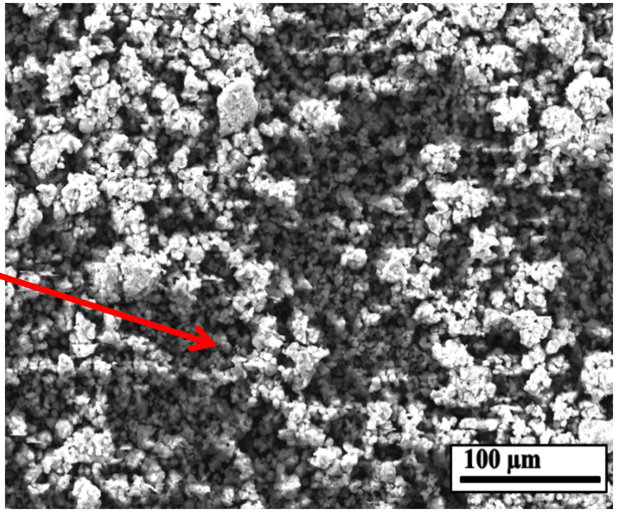


Jampani, P.H.; Gattu, B.; Velikokhatnyi, O.I.; Datta, M.K.; Damle, S.S.; Kumta, P.N. *Journal of the Electrochemical Society*, Vol. 161, pp. A1173-A1180 (2014)



Commercial Sulfur > 40 μm

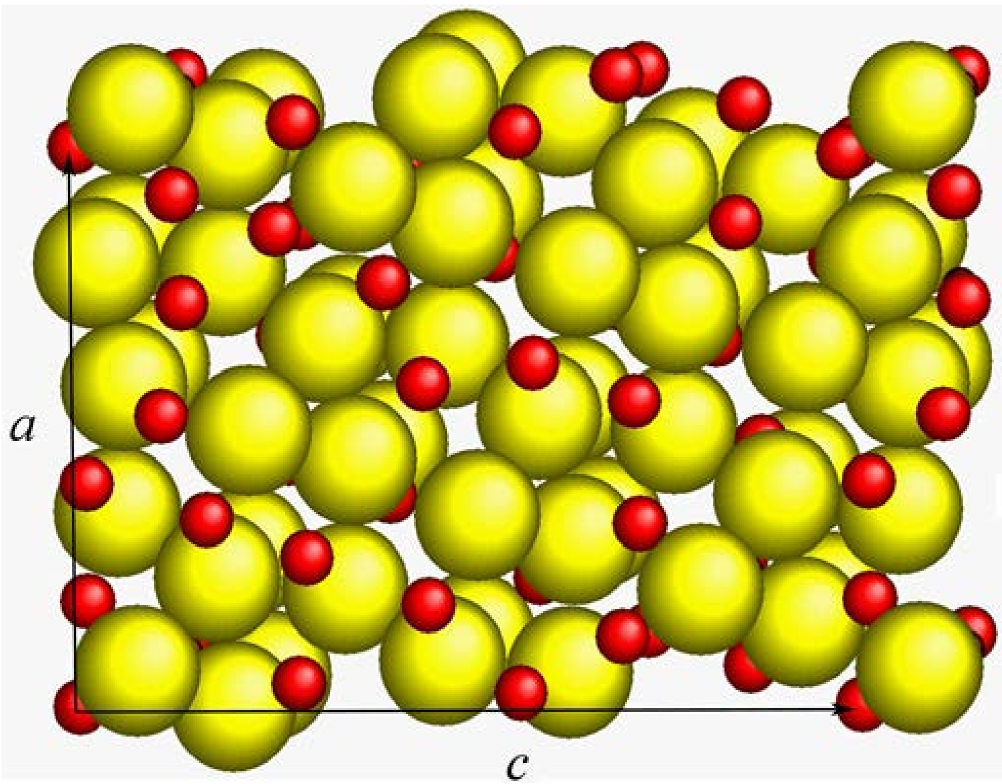




Precipitated Sulfur (aqueous medium) ~200-300 nm

Technical Accomplishments

First principles driven materials selection



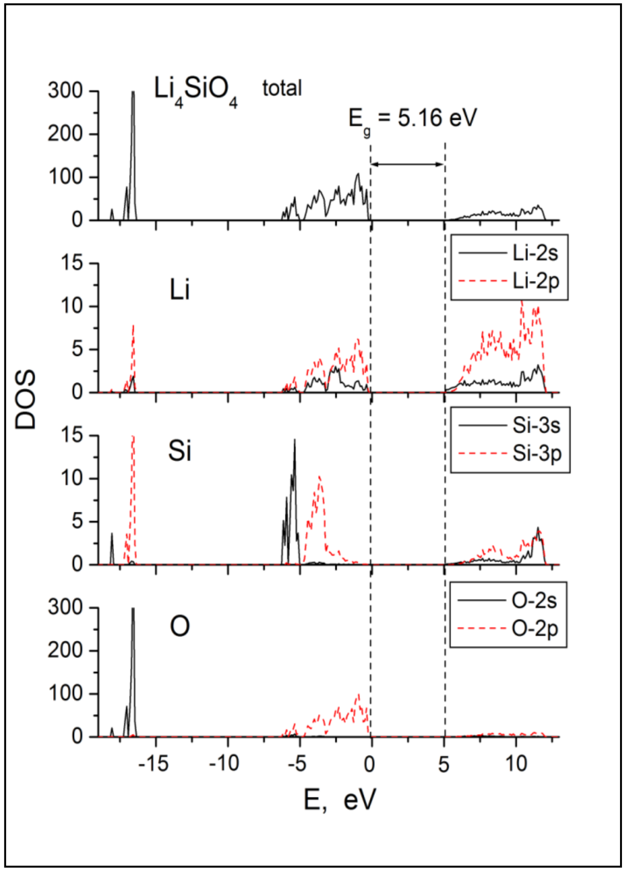
Red: Lithium, Yellow: Oxygen

Embedding sulfur in a sandwich structure consisting of lithium ion conducting solid media

Allows for good ionic contact and conductivity while physically retaining the polysulfides formed in the pores of the conducting matrix

Identification of a Li^+ conducting structure having channels large enough to allow Li^+ to migrate but impermeable to electrolyte molecules

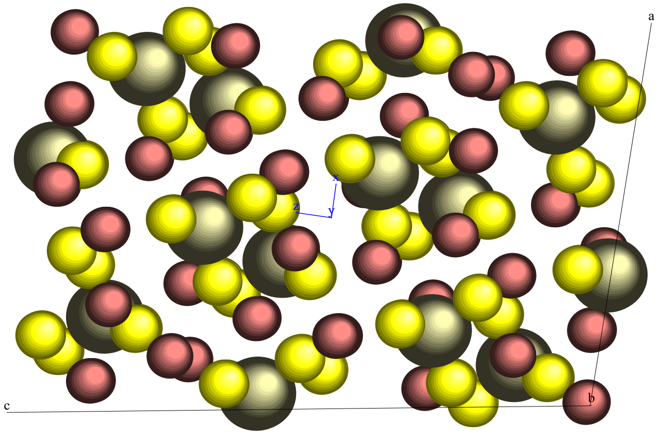
Technical Accomplishments
First principles based design



E_{coh} = 46.6 eV/f.un. or 5.18 eV/at.
(similar to SnO_2 ~5.1 eV/at.)

DFT electronic structure

Li-ion conductivity~ 10^{-8} S/cm



Red - Li; Yellow – Oxygen; Gold – Si
126-atom unit cell

- Very wide band gap insulator
- Strong Si-O hybridization
- Covalent Si-O bonds and ionic Li-O
- Large channels for Li-conduction
- Must be very stable

Technical Accomplishments

Li_4SiO_4 mechanical properties

DFT calculations of elastic constants C_{ij}

C_{11}	C_{12}	C_{13}	C_{15}	C_{22}	C_{23}	C_{25}	C_{33}	C_{35}	C_{44}	C_{46}	C_{55}	C_{66}
120.1	28.9	35.2	2.6	140.8	42.9	-11.7	146.3	-1.0	68.4	-50.2	49.8	32.6

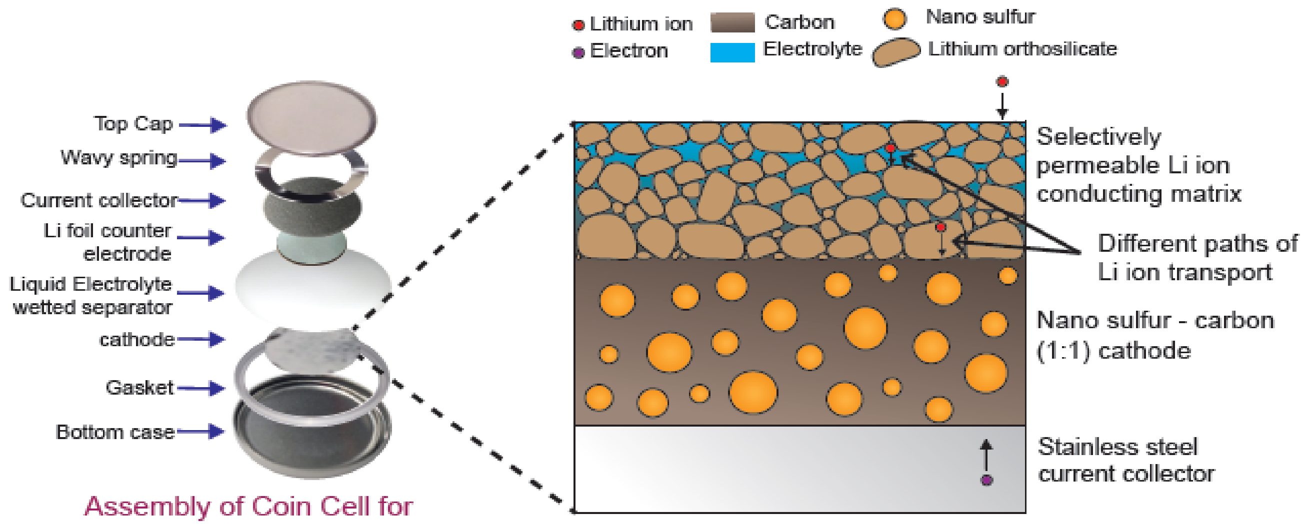
Bulk modulus ***B***, Young's modulus ***E***, and shear modulus ***G***

B **(GPa)**	***E*** **(GPa)**			***G*** **(GPa)**
	E_x	E_y	E_z	
68.5	109.3	121.4	126.2	50.5

- Three elastic constants (C_{25}, C_{35}, and C_{46}) are negative meaning instability of the system to some extent
- Investigation of the origins of such instability and methods for elimination will be the subject of further theoretical study

Technical Accomplishments

Lithium ion conductor (LIC)-Sulfur multilayer composite electrodes (MLCE)



Assembly of Coin Cell for Electrochemical Testing

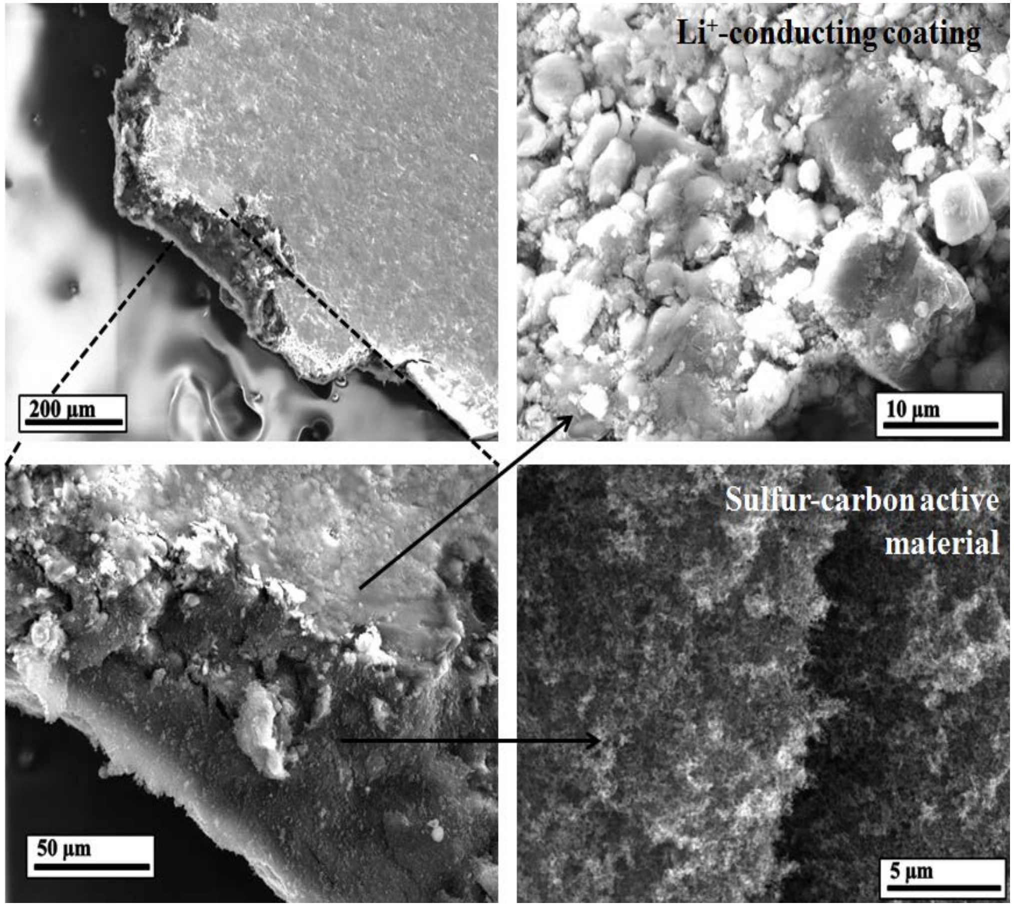
Schematics of the cathode

- Polysulfide species formed during lithiation of sulfur retained at the cathode without dissolution
- Solid-state lithium ion conduction results in minimization of liquid electrolyte contact with sulfur nanoparticles

Jampani, P.H.; Gattu, B.; Velikokhatnyi, O.I.; Datta, M.K.; Damle, S.S.; Kumta, P.N. *Journal of the Electrochemical Society*, Vol. 161, pp. A1173-A1180 (2014)

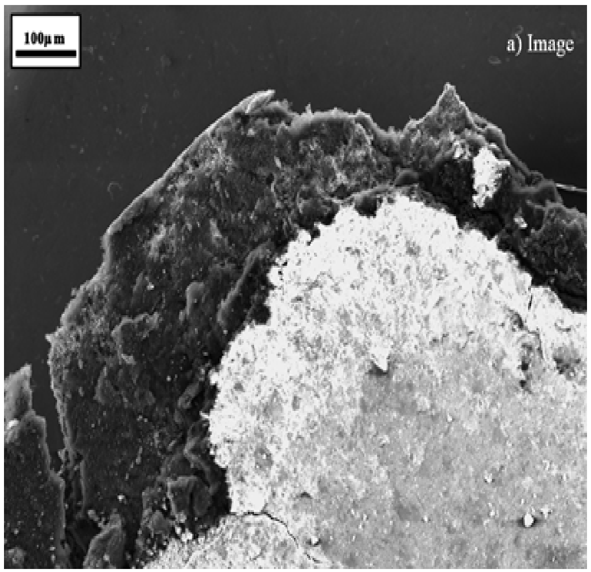
Technical Accomplishments

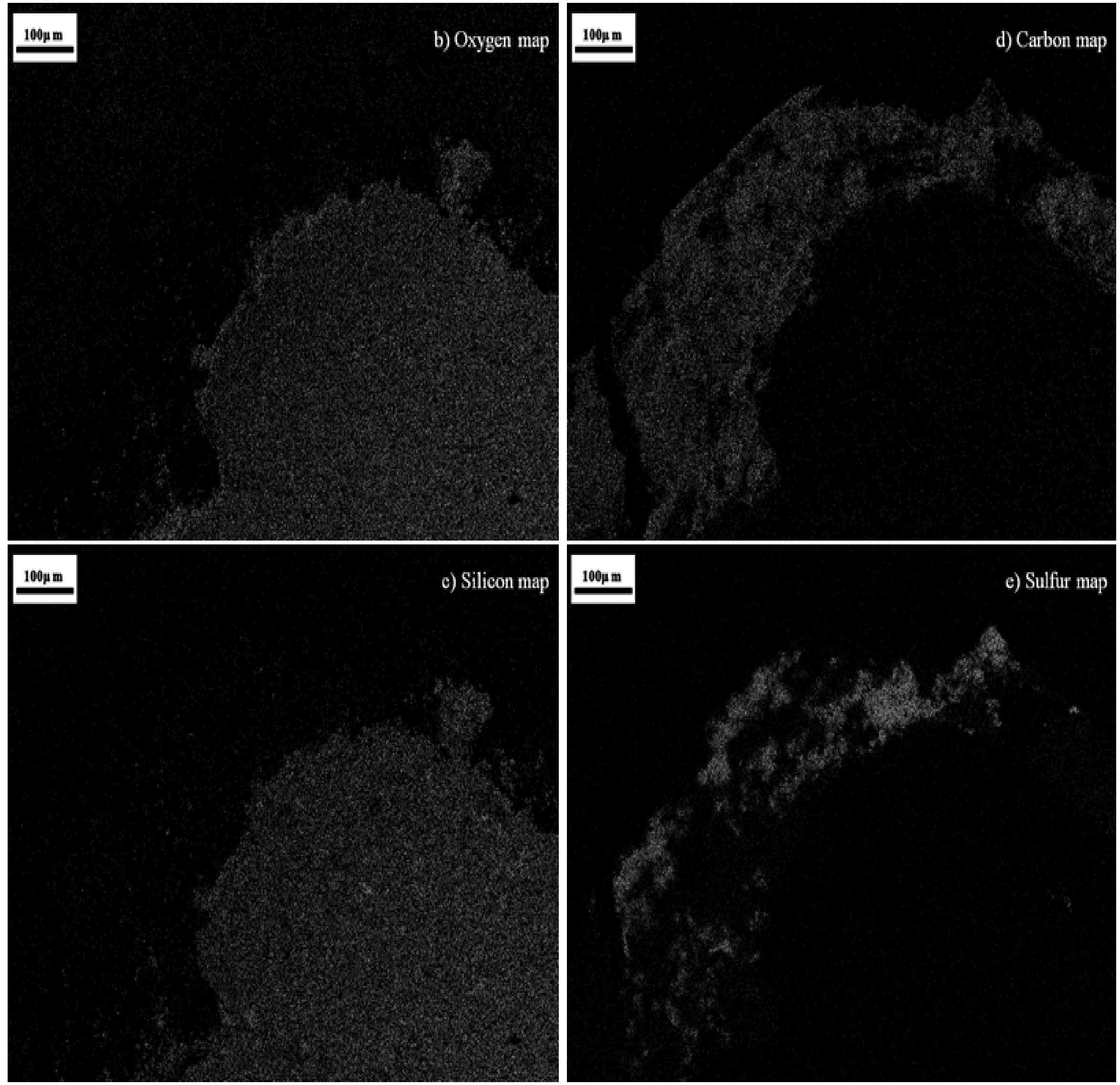
Multilayer composite electrode



Technical Accomplishments

Multilayer composite electrode





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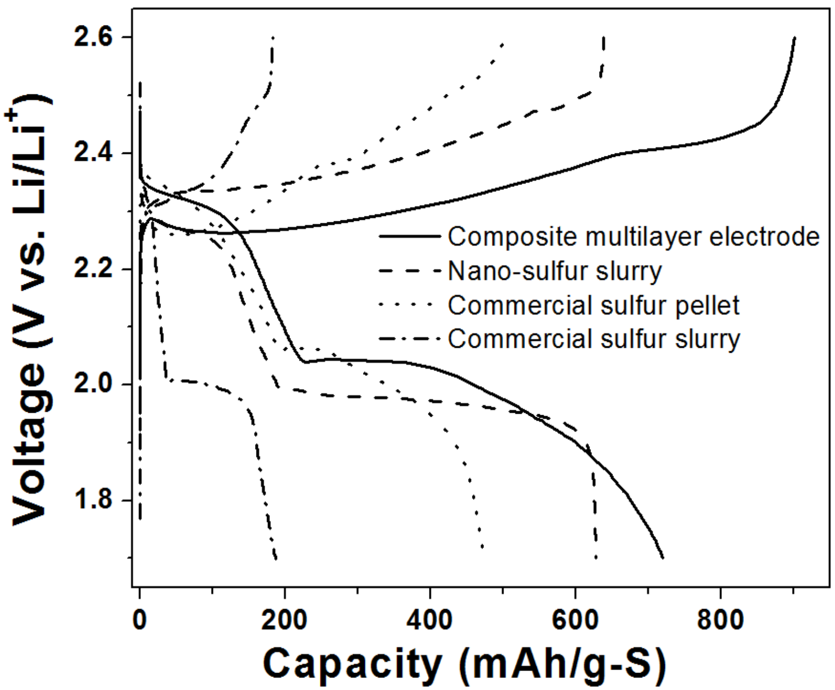
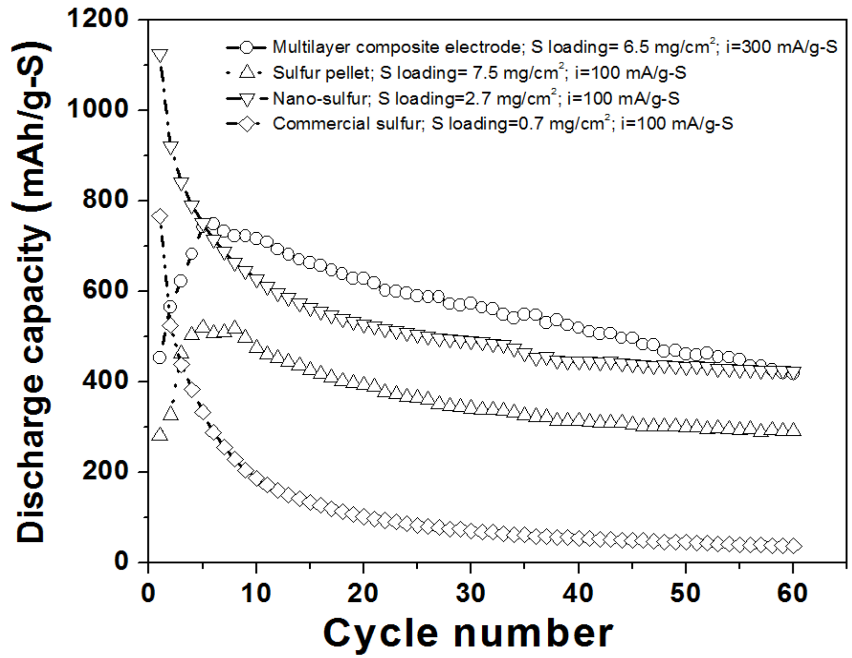
Technical Accomplishments

Electrochemical evaluation





- Characteristic discharge plateaus at ~2.3 V (polysulfide formation) and ~2.1 V (lithium sulfide) observed
- Thicker-higher loading electrodes have more stability than slurry cast electrodes
- Lithium ion conductor results in stabilization of capacity at higher values than that of either slurry based electrodes/LIC-free pellet electrodes

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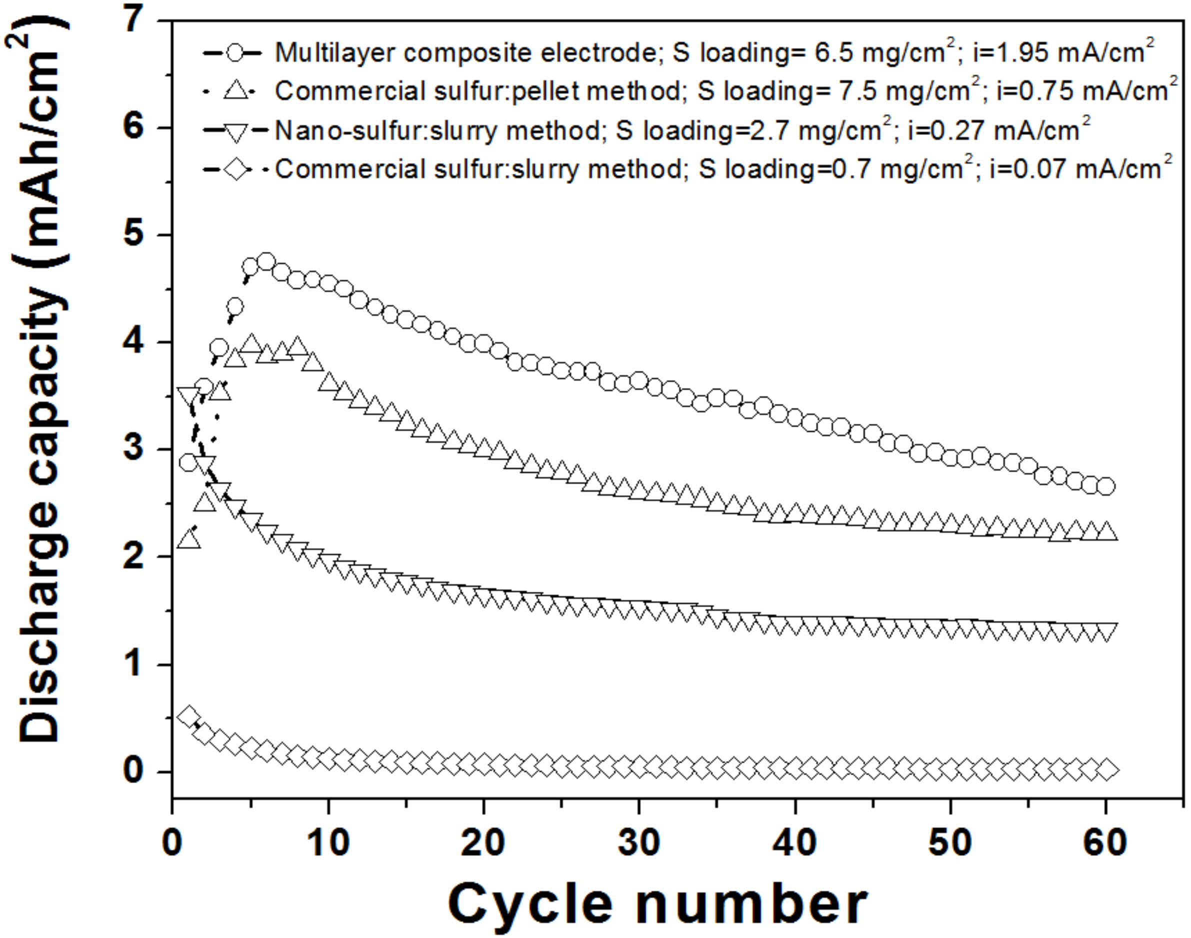
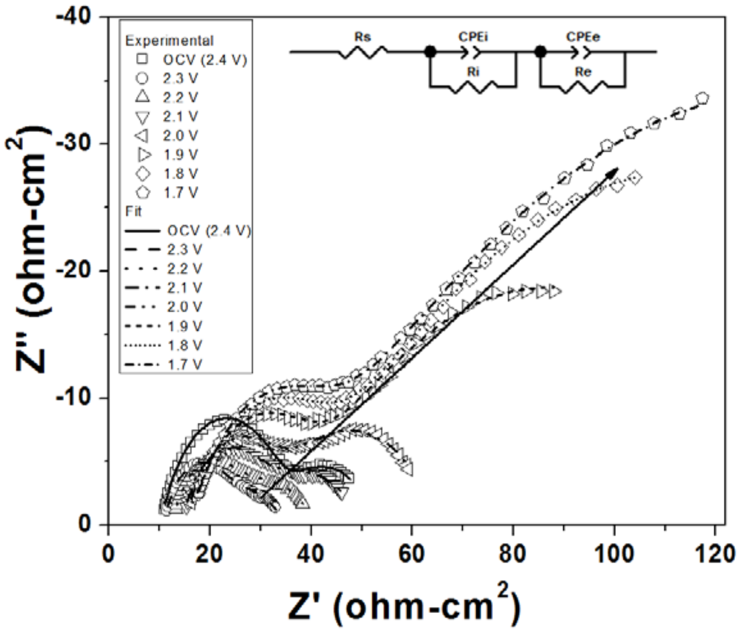
Technical Accomplishments

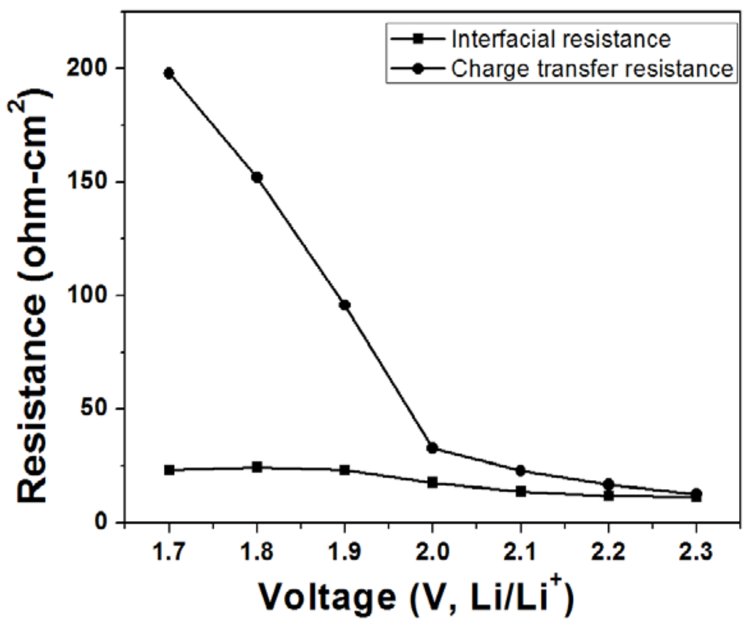
High areal capacity LIC coated MLCE electrodes



Technical Accomplishments

Fundamental electrochemical study to understand the reaction kinetics, mechanism and charge transfer kinetics

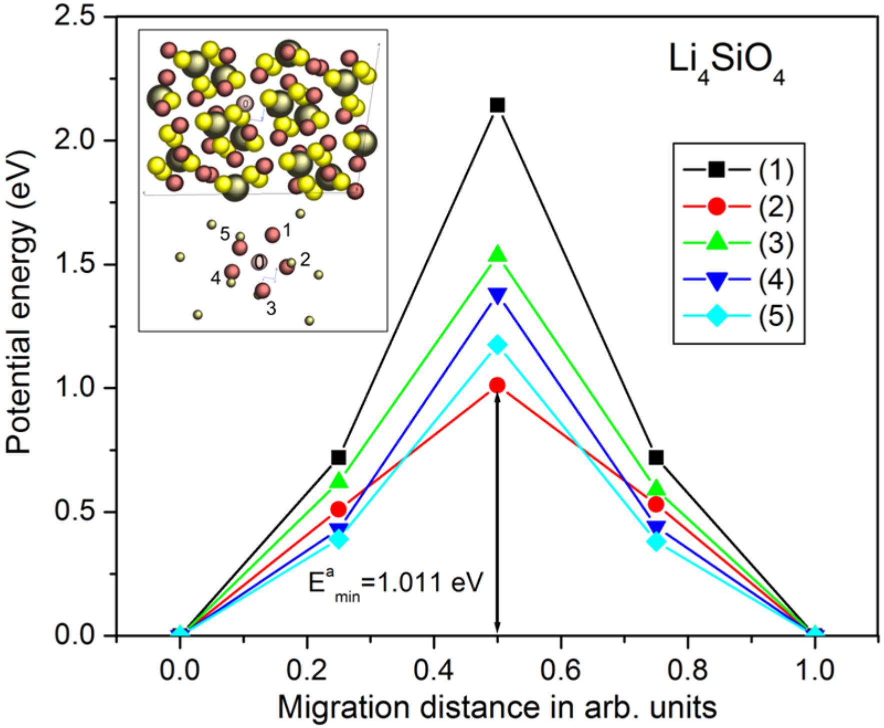




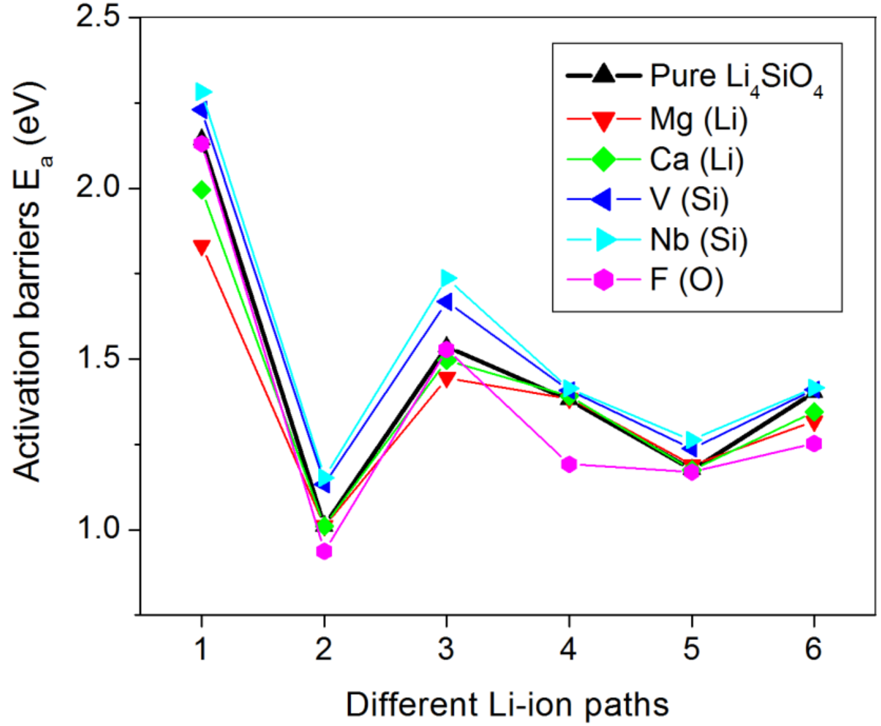
- ➢ Impedance analysis shows initial ease of lithiation to form polysulfide followed by sluggish conversion to Li_2S
- ➢ LIC displays almost constant resistance to lithium ion flow

Jampani, P.H.; Gattu, B.; Velikokhatnyi, O.I.; Datta, M.K.; Damle, S.S.; Kumta, P.N. *Journal of the Electrochemical Society*, Vol. 161, pp. A1173-A1180 (2014)

Technical Accomplishments
Doping of LIC materials



Activation barriers for different migration paths of Li-ions in Li_4SiO_4. Inset: pink 0 - Li-ion site; red (1)-(5) – Li vacancy sites for different migration pathways.

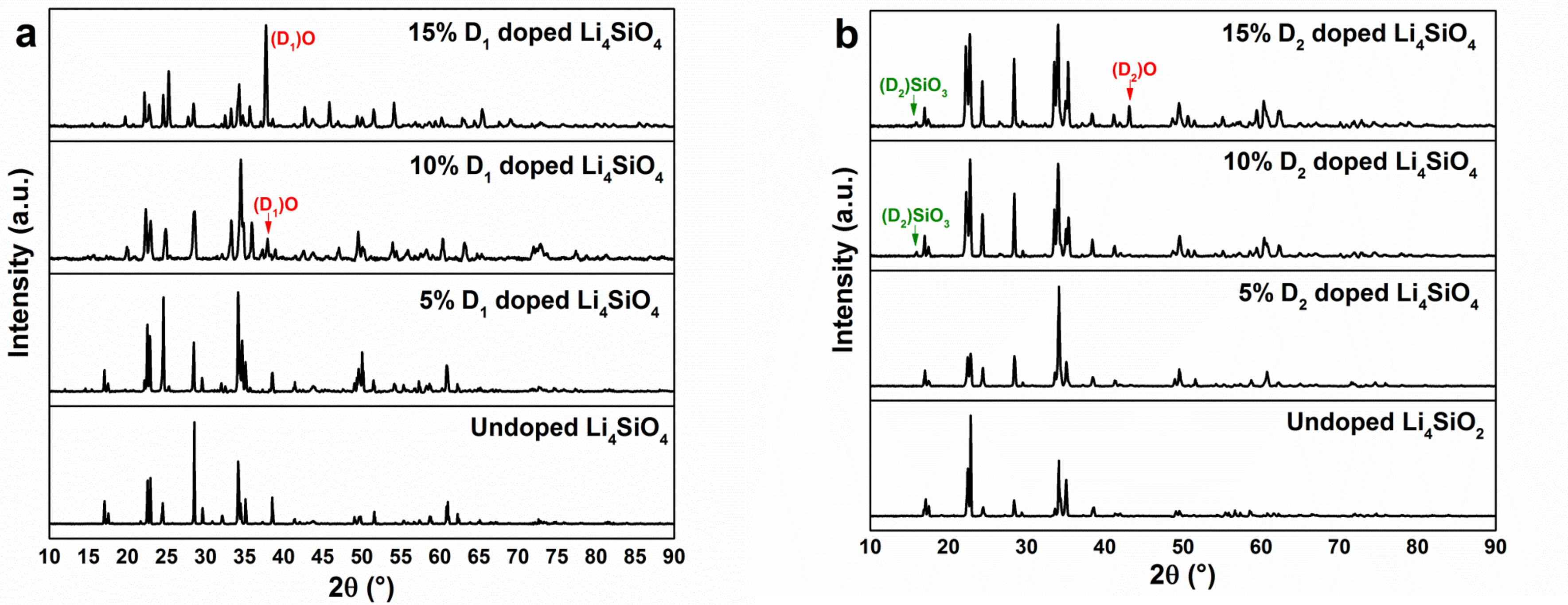


Activation barriers E_a for different migration paths of Li-ions in pure and doped Li_4SiO_4.

- Using the nudged elastic band method implemented in VASP (Vienna ab-initio simulation package), various Li-ion migration pathways have been considered and corresponding activation barriers E_a have been calculated

Technical Accomplishments

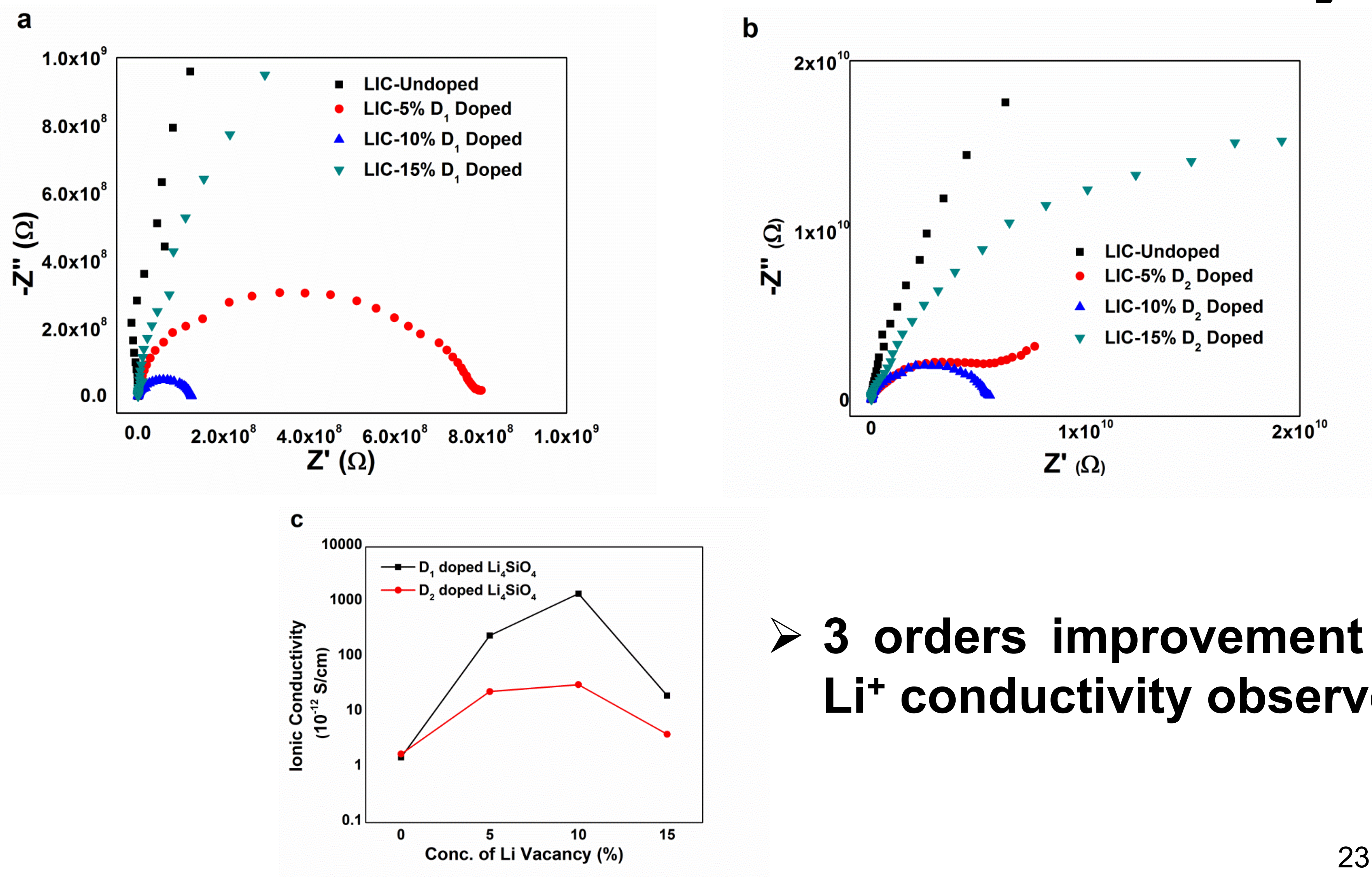
Doping of LIC materials



➢ **Doping up to 10% successfully accomplished**

Technical Accomplishments

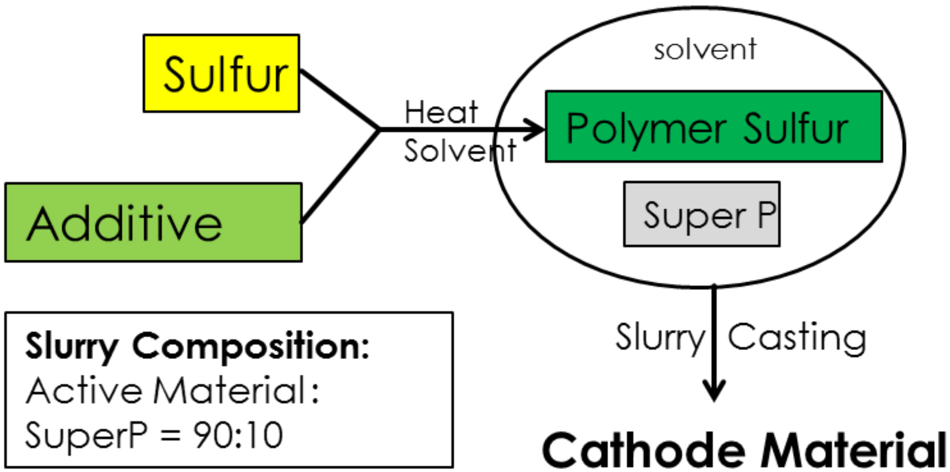
Improvement in ionic conductivity



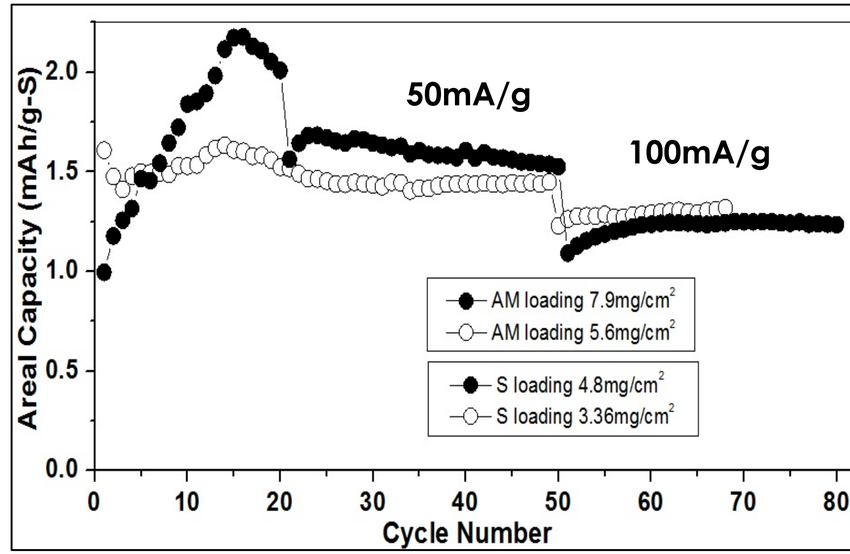
- 3 orders improvement in Li^+ conductivity observed

Technical Accomplishments

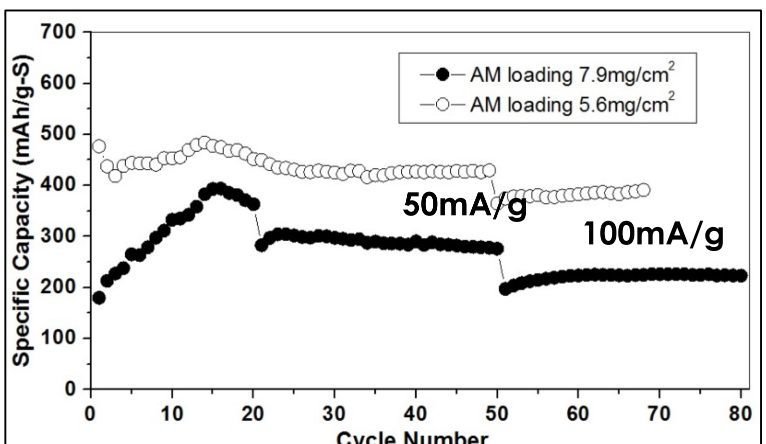
Binderless Polymer Sulfur



Slurry Composition:
Active Material:
SuperP = 90:10



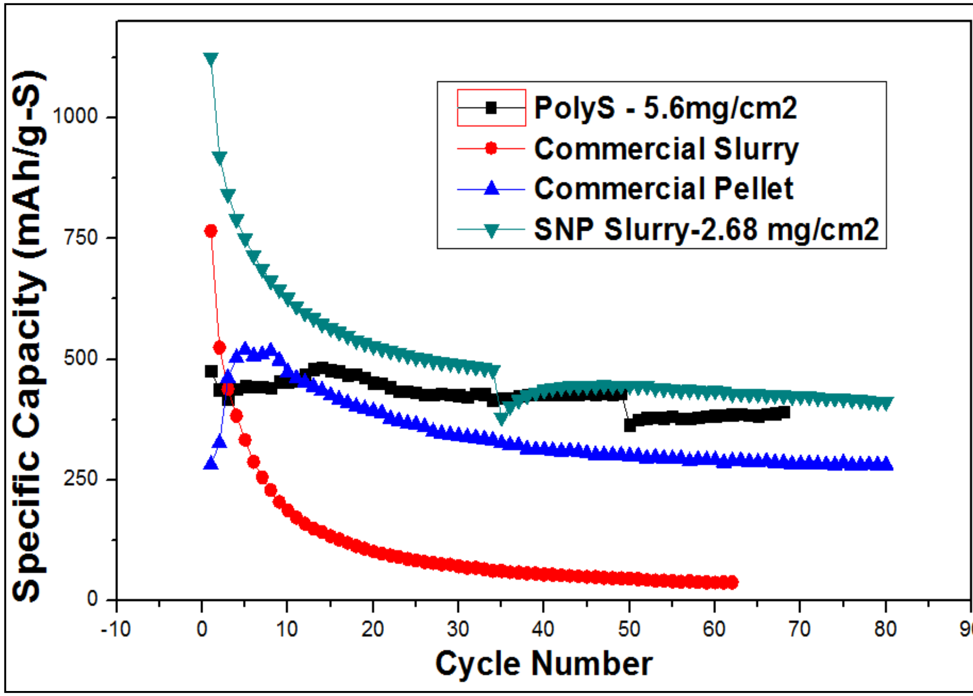
Binderless method:
Polysulfur acts as binder along with preventing dissolution phenomenon.

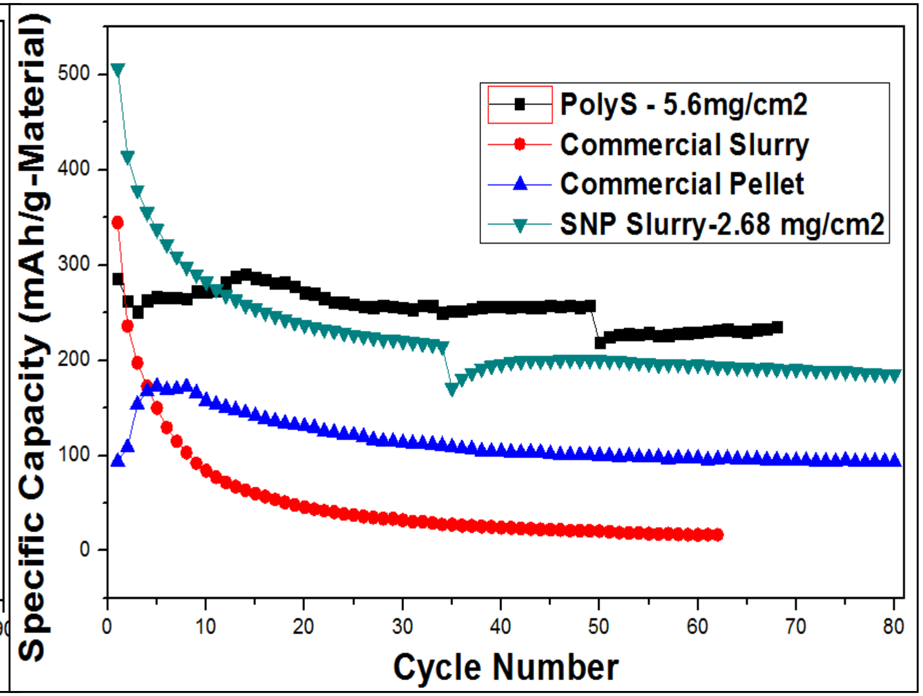


- ✓ Specific capacity of 450 mAh/g with respect to sulfur and 315 mAh/g with respect to active material till 50 cycles
- ✓ Stability in cycling
- ✓ Easy one pot synthesis with cheap precursors

Technical Accomplishments

Binderless Polymer Sulfur

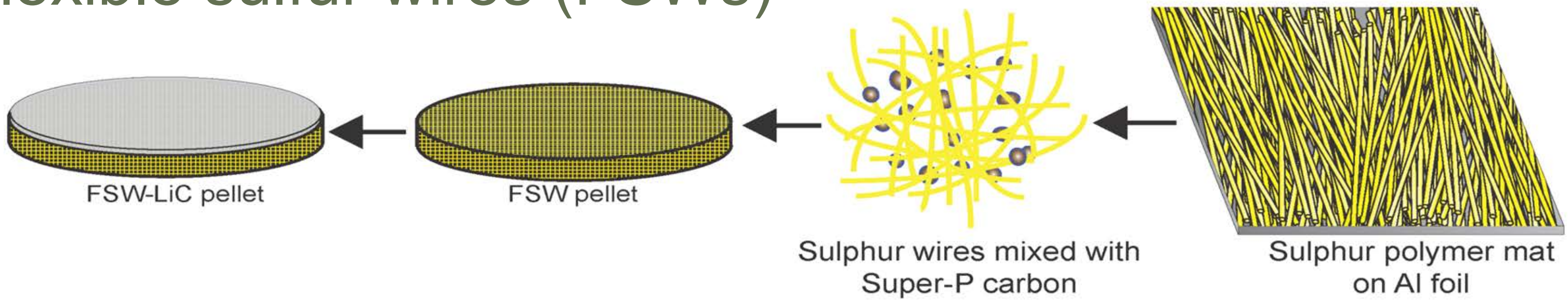




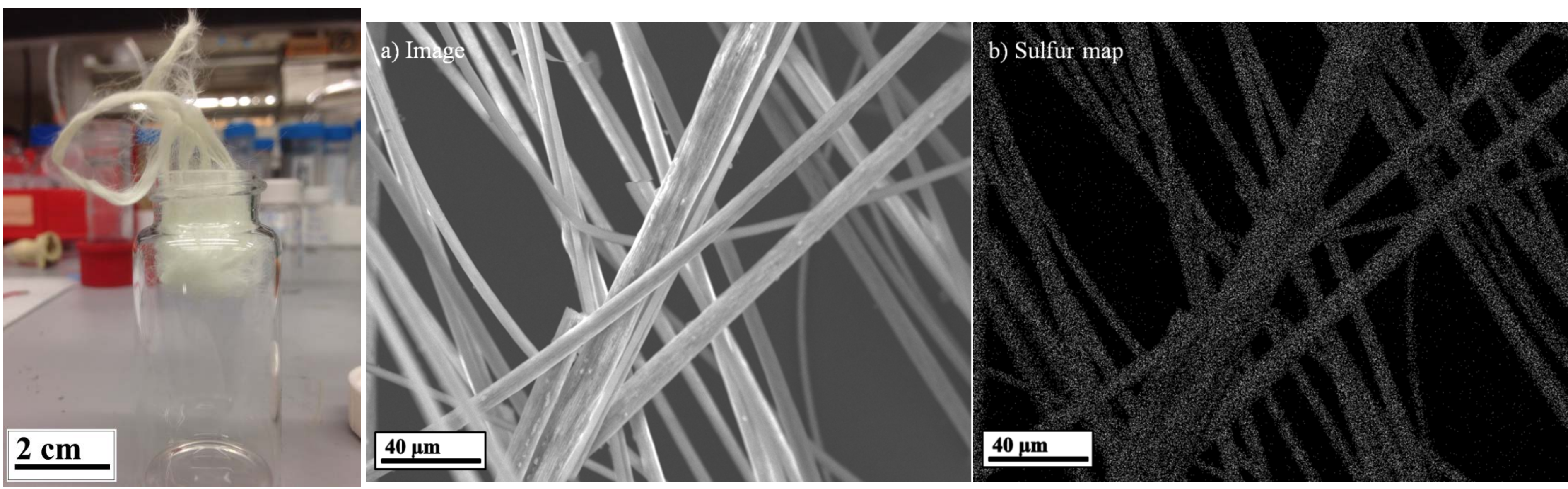
- ✓ Better stability than commercial and sulfur nanoparticles
- ✓ Higher specific capacity on the basis of total weight for Poly Sulfur as compared to others
- ✓ Performance and specific capacity on the basis of sulfur comparable to nanosulfur
- ✓ Higher loadings as compared to nanosulfur slurry
- ✓ Loadings can be easily improved for Poly sulfur by using higher thickness during tape casting

Technical Accomplishments

Flexible sulfur wires (FSWs)

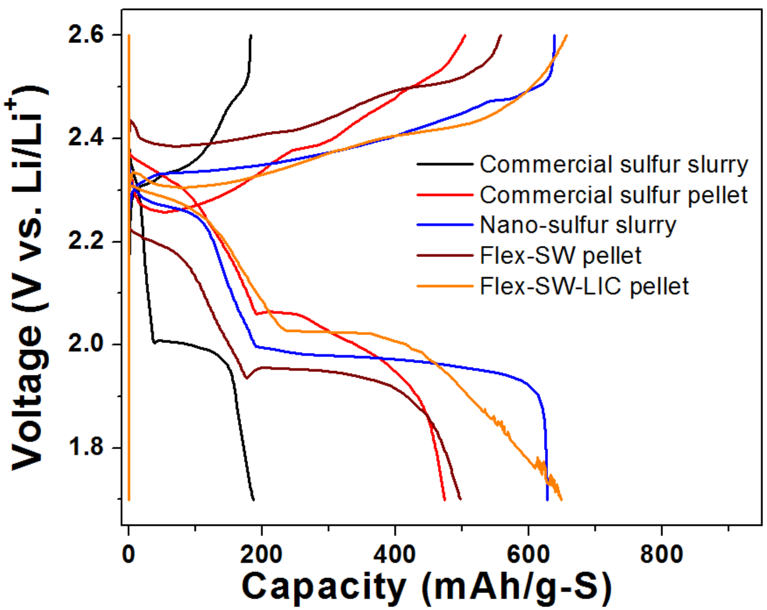


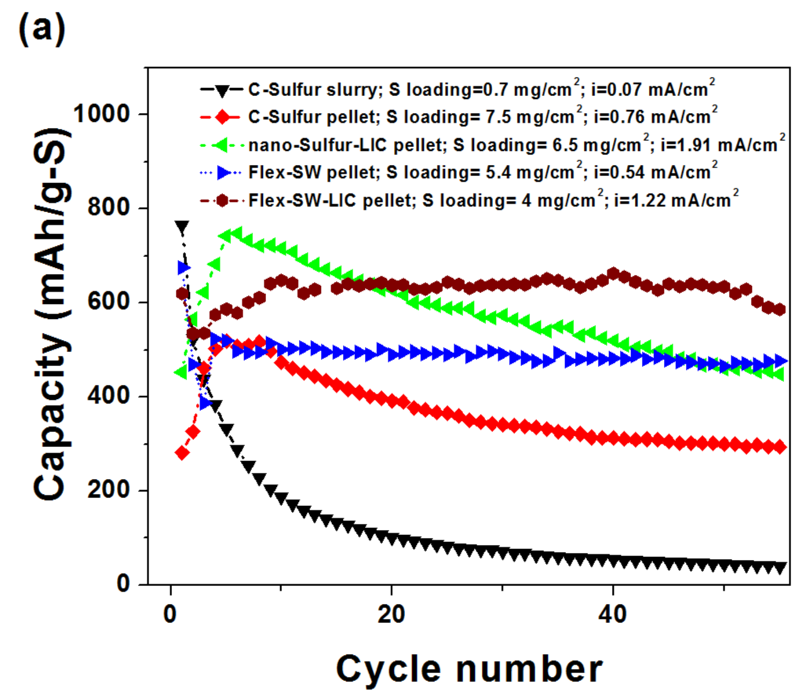
- Flexible sulfur wires made by simple chemical processing
- Act as both conductive matrix and polysulfide retention media
- Amenable for flexible energy storage applications



Technical Accomplishments

Flexible sulfur wires (FSWs)-Performance

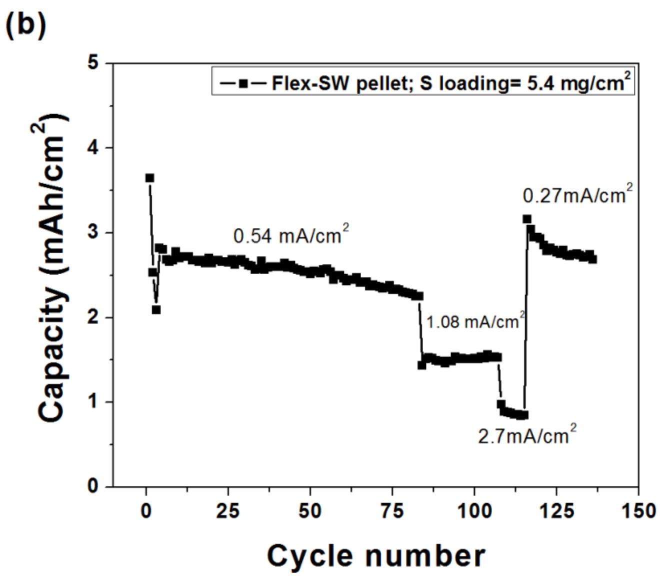




- **Flexible sulfur wires demonstrate stable charge storage behavior over ~150 cycles at different rates**
- **Initial loss in capacity occurs possibly as a result of contact of surface sulfur species with liquid electrolyte**
- **High areal capacities of ~2.5-3 mAh/cm^2 at high current densities**

Technical Accomplishments

Flexible sulfur wires (FSWs)



- **Exceptionally low fade rate of ~0.003 %/cycle observed**

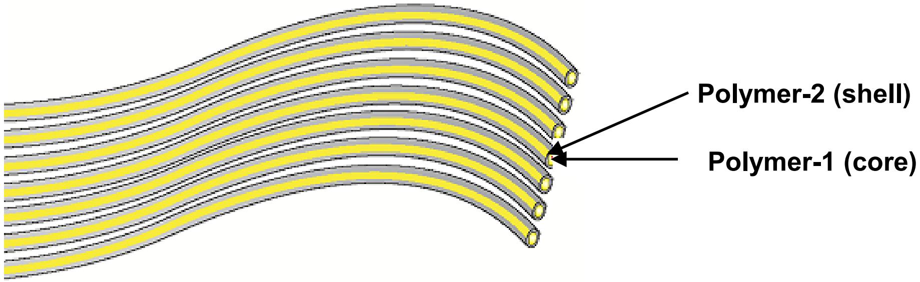
Materials	Flex – SW pellet	Flex – SW – LIC pellet	Sulfur cathode	Conventional lithium battery cathodes
Gravimetric capacity (mAh/g-S)	450-500	600-650	300-1200	
Gravimetric capacity (mAh/g-active material)	~100	150-200	200-400	150-225
Areal capacity (mAh/cm²)	2-3	2-3	2-	0.5-1
Cycling fade rate (%/cycle)	0.17	0.003	0.04-0.2	0.2

Technical Accomplishments

Polymer based Approach – Lithium ion Conducting Membrane (LICM)

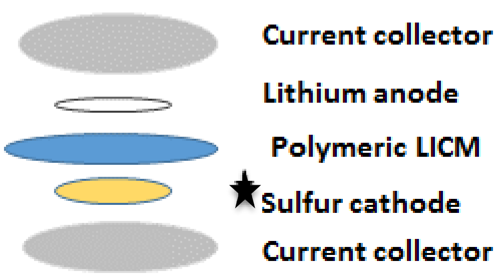
Polymer Systems	Room temperature conductivity (mS/cm)	Disadvantages
Liquid electrolyte (EC:DMC: 1M $LiPF_6$)	6-7	Polysulfide dissolution
Polymer- 1	2.57	Poor compatibility with Lithium/ Passivation on contact
Polymer- 2	0.375	Poor mechanical strength

Combining high conductivity of Polymer-1 and compatibility of Polymer-2



Polymer-2, Polymer- 1 core-shell fiber morphology

Polymer- 1, Polymer- 2 layered fiber morphology

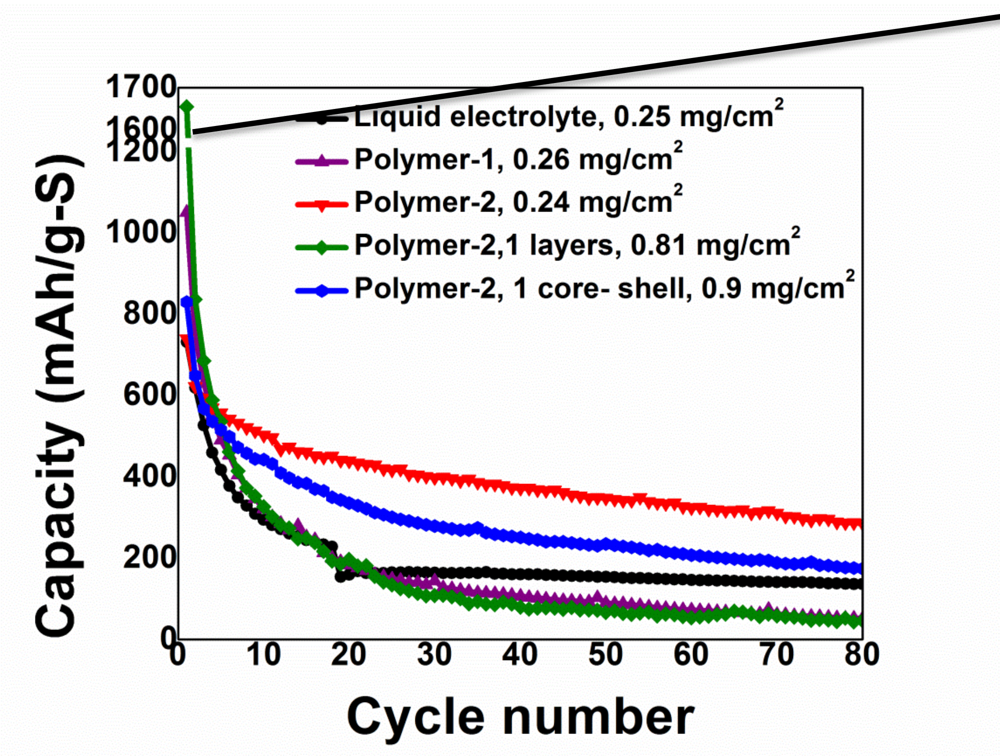


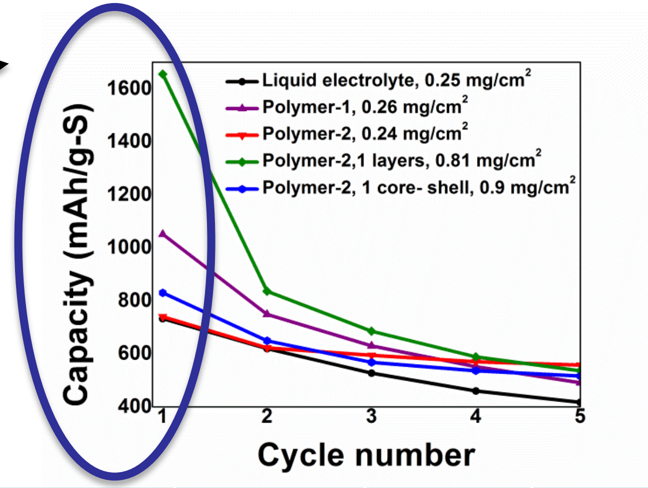
Testing polymeric LICM

★ P J Hanumantha, B Gattu, O Velikokhatnyi, M K Dutta, S S Damle, P N Kumta, J. Electrochem. Soc., 161(6), A1173-1180

Technical Accomplishments

Electrochemical Cycling behavior





Cycling behavior of polymer electrolytes with different morphologies

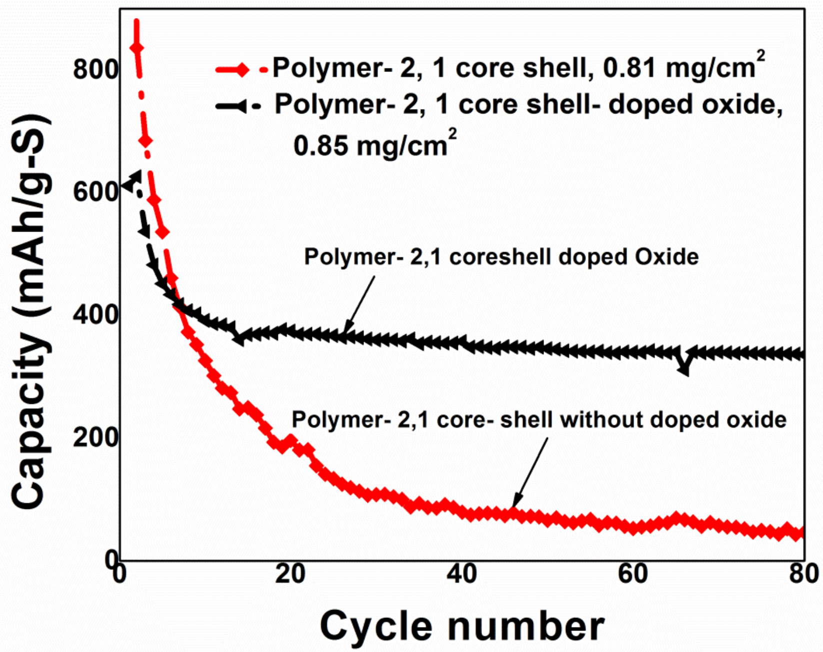
System	Ini. Dis. Cap (mAh/g)	First Cycle IRL (%)	Fade rate/ cycle (%)
Liquid electrolyte	732.27	15.42	1.53
Polymer-1	1051.08	28.77	1.79
Polymer- 2	739.52	15.80	1.15
Polymer- 2, 1 layers	1654.88	49.46	1.87
Polymer- 2, 1 core shell	829.96	21.71	1.30

- Use of polymeric layers results in reduction in polysulfide dissolution

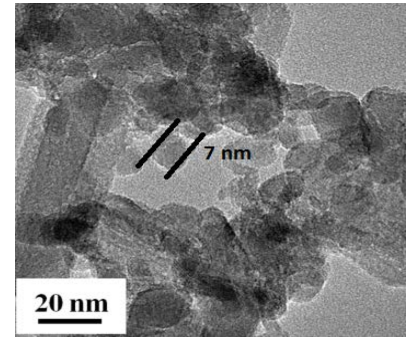
Technical Accomplishments

Oxide doping in LICM material

Doped Oxide incorporated Polymer- 2, 1 core-shell system – stabilized at ≈400mAh/g after 80 cycles



Cycling behavior of polymeric LICM with doped oxide nano- filler



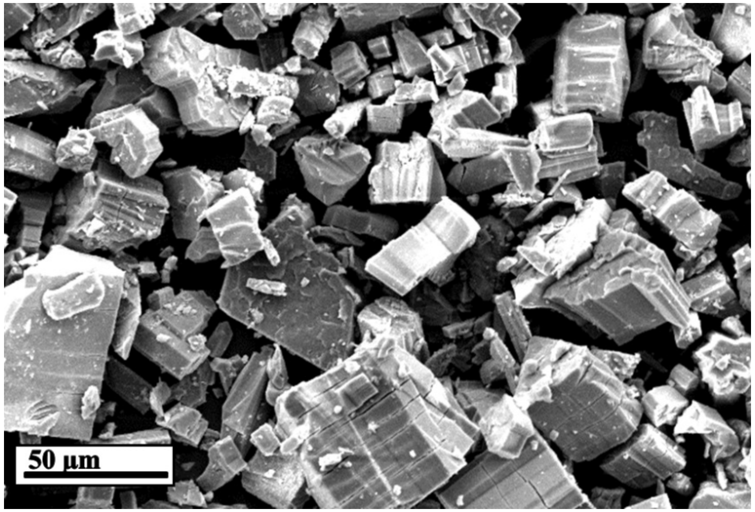
System	Ini. Dis. Cap (mAh/g)	First Cycle IRL (%)	Fade rate/ cycle (%)
Polymer- 2, 1 layers	1654.88	49.46	1.87
Polymer- 2, 1 core shell	829.96	21.71	1.30
Polymer- 2, 1 core shell- doped oxide	624.49	2.08	0.86
Polymer- 2, 1 layers- doped oxide	776.41	19.3	1.02

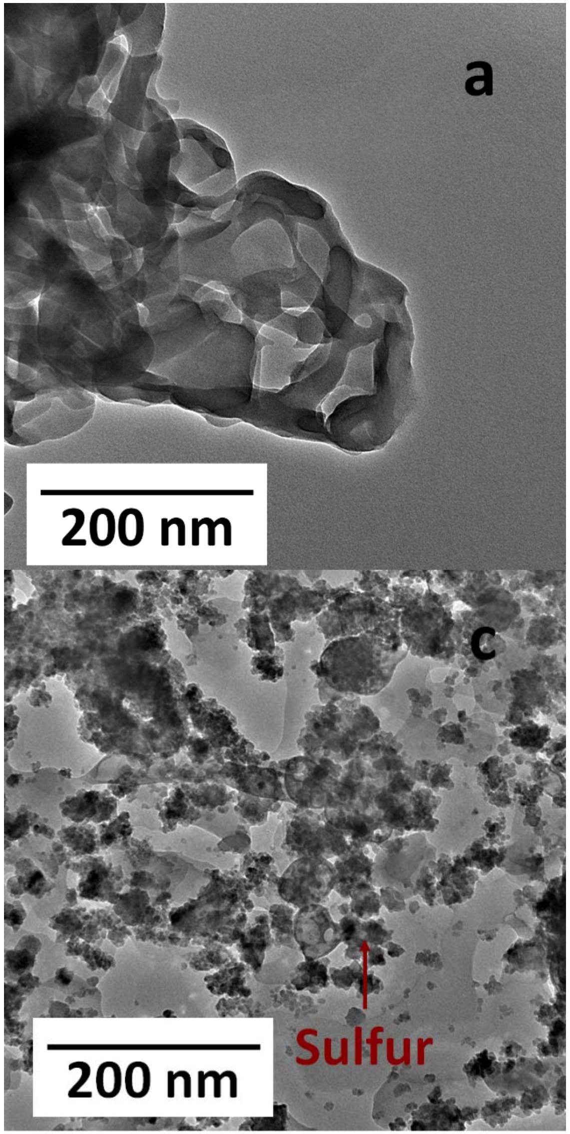
Lowest irreversible capacity loss

- Use nanofillers improves cycling stability

Technical Accomplishments

Nanoporous Complex Framework Materials(CFM) approach

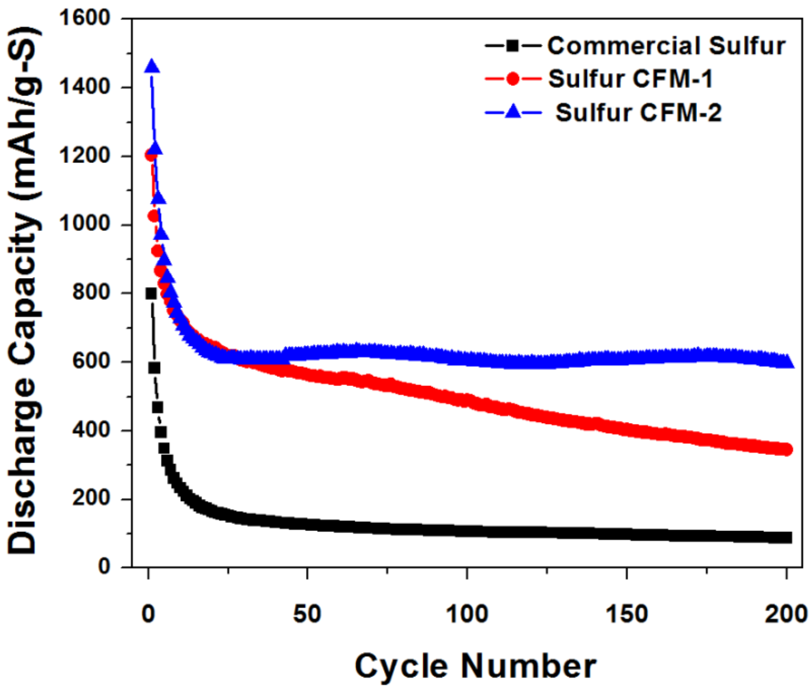


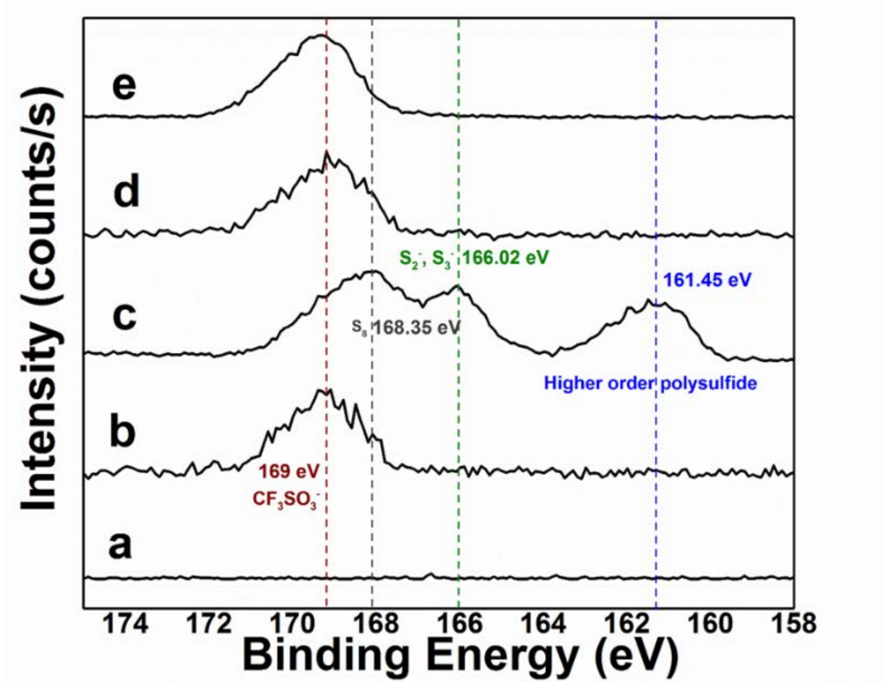


	BET Surface Area (m^2/g)	Langmuir Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Adsorption average pore width (Å)
CFM-1	525.98	829.18	0.324	2.46
CFM-2	684.25	1083.07	0.422	2.47

Technical Accomplishments

Electrochemical behavior of CFM materials





- ➢ Improvement in cycling stability of sulfur cathodes by use of CFM materials

XPS S2p Binding Energy profile of a) commercial separator b) commercial separator soaked in electrolyte; separators of c) commercial sulfur electrode d) Sulfur CFM-1 e) Sulfur CFM-2 electrodes; (after 200 cycles at 0.2 C rate)

Responses to Previous Year Reviewers' Comments

- The project was not reviewed last year. Hence there are no comments.

Collaboration and Coordination with Other Institutions

- Collaborators (outside the VT Program):
  - Dr. Spandan Maiti (University of Pittsburgh): for mechanical stability and multi-scale modeling
  - Dr. A. Manivannan (NETL): for x-ray photoelectron spectroscopy (XPS) for surface characterization
  - Dr. D. Krishnan Achary (University of Pittsburgh):for solid-state nuclear magnetic resonance (MAS-NMR) characterization

Remaining Challenges and Barriers

- **Challenges**
  - Synthesis of sulfur nanoparticles with high electronic conductivity to reduce additive weight and increase energy density
  - Coating of LIC on sulfur nanoparticles
  - Interface engineering and coating of sulfur on Carbon Nanotubes (CNTs) – LIC composite structures
- **Barriers**
  - No significant barriers to proposed work has been encountered thus far
  - Possible barriers include accounting for scaling of performance and increasing sulfur weight percentage in electrodes
- **Solutions**
  - Optimization using effective additives and incorporation of CNT

Proposed Future Work
Electronic modification of Sulfur

- First principles driven alteration of sulfur to improve electronic conductivity and reaction kinetics
- Coating of LIC materials on sulfur nanoparticles
- Use of composite LIC-coated CNT-sulfur nanostructures
- Large electrode fabrication and testing
- Final deliverable of 4 mAh cell

Upcoming key milestones

- Fundamental electrochemical study to understand the interface electrochemical properties such as change of charge transfer resistance, Li^+ diffusivity and electronic conductivity
- Synthesis of modified sulfur nanoparticles with high electronic conductivity to reduce additive weight and increase energy density.
- Design and engineering of high capacity LIC coated sulfur nanoparticles for generation of high capacity materials for targeted energy density and 4 mAh cell

Summary

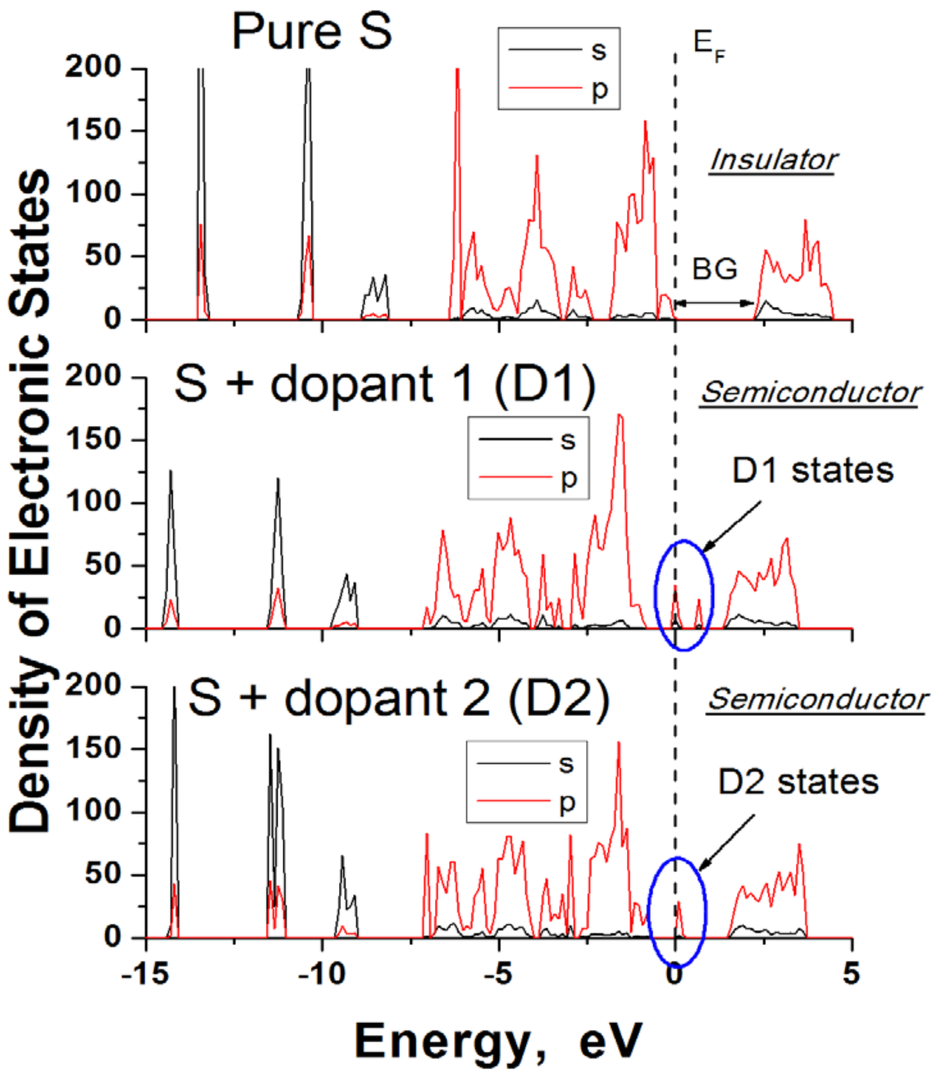
Cycling characteristics of various sulfur battery systems synthesized and evaluated in this work.			
Materials	**Initial discharge capacity (mAh/g-S)**	**Initial capacity fade¥ (% capacity)**	**Fade rate* (% capacity/cycle)**
C-Sulfur:slurry	766.3	56.53	1.76
C-Sulfur pellet	519.3†	N/A	0.87
nano-Sulfur-LIC pellet	748.2†	N/A	0.79
Flex-SW pellet	675.4	23.09	0.17
Flex-SW pellet-LIC	620.3	5.37	0.003
Polymer 2,1 core-shell-doped oxide	776.26	36.75	0.4
Sulfur CFM-2	1460.4^	54.79	0.01

¥Fade rate calculated on the basis of 1st cycle capacity and 5th cycle capacity.*Fade rate calculated on the basis of 5th cycle capacity and 55th cycle capacity. †Capacity reported at 5th cycle since there was an increase in capacity from 1st cycle due to gradual wetting of the electrode.^Stabilizes at 20th cycle and fade calculated upto 200th cycle.

- Sulfur cathodes with very high capacities demonstrated and exceptionally low fade rates of <0.01%/cycle demonstrated in Sulfur-CFM materials and Flex-SW-LIC pellet materials
- Cycling behavior demonstrated for up to 300 cycles with further cycling ongoing

Technical Back-Up Slides

Electronic modification of Sulfur



First principles driven alteration of electronic states of sulfur to improve electronic conductivity